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Final report, PSO-Eltra 4766

Zheng, Yuanjing; Jensen, Peter Arendt; Jensen, Anker Degn; Sander, Bo; Junker, Helle

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Department of Chemical Engineering
Technical University of Denmark
Building 229
DK-2800 Lyngby
Denmark



Ash transformation in suspension fired boilers co-firing coal and straw

Final report, PSO-Eltra 4766

**Yuanjing Zheng^a, Peter Arendt Jensen^a, Anker Degn Jensen^a, Bo Sander^b, Helle
Junker^b**

^aDepartment of Chemical Engineering, Technical University of Denmark, Building 229,
DK-2800 Kgs. Lyngby, Denmark

^bDONG Energy A/S, Kraftværksvej 53, DK-7000 Fredericia, Denmark

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Abstract

The properties of the ash from co-firing of coal and straw have a large influence on boiler operation, flue gas cleaning equipment and appropriate utilization of the fly ash. A study on the fuel composition and local conditions influence on fly ash properties has been done by making entrained flow reactor experiments with co-firing of coal and straw, making mineral and alkali vapor laboratory reactor experiments and by developing a model of KCl reaction with kaolin. The results include correlations that can be used to estimate the speciation of potassium in the fly ash when co-firing straw and bituminous coal. The laboratory experiments indicated which mineral types and local conditions that provide the most efficient binding of potassium to species with a high melting point, and where a simultaneous release of chlorine as gaseous HCl takes place.

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- A. Literature review of ash transformation during co-firing coal and straw, Zheng Y, Jensen P A, Jensen A D (2005)
- B. Ash transformation during co-firing coal and straw, Zheng Y, Jensen P A, Jensen A D, Sander B, Junker H, Fuel 86 (2007) 1008-1020.
- C. A kinetic study of gaseous potassium capture by coal minerals in a high temperature fixed bed reactor, Zheng Y, Jensen P A, Jensen A D. Fuel 87 (2008) 3304-3312.
- D. Potassium capture by kaolin and fly ash powder in an entrained flow reactor, Zheng Y, Jensen P A, Jensen A D (2007).

1.0 Introduction

Co-firing straw with coal in existing large-scale pulverized fuel boilers offers several advantages over grate boilers fired exclusively with biomass, such as lower investment costs and a higher electrical efficiency. However, co-firing coal with straw raise some technical challenges due to the ash composition of straw. Most of the problems that may arise during coal and straw co-firing are due to the high content of potassium and chlorine in the straw. Possible straw ash induced problems include boiler deposit formation, corrosion, deactivation of SCR catalysts and problems with adequate fly ash utilization. A major barrier for more widespread use of co-combustion installations in Denmark is related to the marketability of the fly ash residues. Power plant fly ash can be utilized in cement or concrete production and thereby expensive dump storage can be prevented.

Current building material standards such as EN 450 and EN 197-1 restrict the use of co-firing fly ash in concrete and cement. To more widely spread the co-firing technology, the new standard EN450-1 allows to co-fire maximum 20 wt% of biomass if the requirements of the fly ash quality can be met. The required contents of total alkali, Cl and residual carbon for fly ash to be used in concrete production are 5 wt%, 0.1 wt%, and 5 wt%, respectively. It is therefore important to have some capability to predict the chlorine and alkali contents of co-firing fly ashes.

The chlorine content of the fly ash and the speciation of potassium in the fly ash are strongly influenced by reaction of the straw ash with coal ash and coal sulfur. The speciation of potassium to a large degree determines important properties of fly ash and ash deposits. Potassium mainly appears in the components listed below, and also the boiler operation problems associated with the different components are shortly summarized here:

1. KCl: A fly ash with a high KCl content can induce problems with large amount of ash deposit formation, high boiler corrosion, and impediment of fly ash utilization because of a high Cl content in the fly ash. Accelerated deactivation of de-NO_x catalysts during coal and straw co-firing may take place if significant amounts of KCl are present in the fly ash.
2. K₂SO₄: If potassium appears as potassium sulphates less problems with boiler corrosion and ash utilization are observed. Deactivation of SCR catalyst still takes place.
3. K-silicates: If potassium appears as silicates the deactivation of SCR catalysts is prevented, but alkali silicates do have relatively low melting temperatures so severe deposit formation may be a problem.
4. K-aluminum-silicates: The melting temperature of this ash is higher than that of potassium silicate and a less troublesome deposit is formed.

In all cases where the dominant species are others than KCl most chlorine will be emitted from the boiler as HCl in the flue gas.

It is important when co-firing biomass and coal to have tools that can be used to predict the properties of the generated fly ash both to minimize operational problems and to make an appropriate utilization of the fly ash. This project was initiated to improve our

understanding of the formation of fly ash when co-firing straw and coal. The main goals of the project were:

- To understand interactions between coal ash and coal sulfur and K, Cl from straw.
- To investigate the influence of coal quality on ash deposit and fly ash composition during coal/straw co-firing.
- To improve predictions of K, Cl, and S contents in the fly ash from coal and straw co-combustion.
- To study the agreement between full-scale and CHEC pilot-scale entrained flow reactor co-firing tests concerning ash composition.
- To obtain kinetics and mechanisms of potassium capture by alumina silicates and to develop a mathematical model of the gas-solid reaction between potassium vapor and coal minerals.

The project was conducted by performing both experimental and theoretical studies. As a basis for the work a literature review of ash transformation during coal and straw co-firing was performed. An experimental investigation of straw co-firing with different ranks of coal in the entrained flow reactor was performed, the results were compared with full-scale co-firing data and empirical correlations describing the fly ash content of K, Cl and S as a function of the fuel ash mix composition were developed. A fundamental experimental study of potassium capture by coal minerals in a lab-scale fixed bed reactor at temperatures relevant to the pulverized fuel combustion was performed, and a mathematic model of gas-solid reaction between potassium chloride vapor and cylindrical kaolin pellets was developed. Last, an experimental investigation of potassium capture by kaolin and coal fly ash powders was done by feeding KCl/kaolin and KCl/fly ash mixture in an electrically heated entrained flow reactor.

This report summarizes the results of the work performed. Detailed documentation and results are presented in the appendixes.

2.0 Literature review

The literature regarding straw and coal ash behavior was reviewed. Straw has much smaller sulfur content but larger content of chlorine and potassium when compared to coal. During 100% straw combustion a lot of KCl is formed which induce high rates of deposit formation, boiler tube corrosion and provides a fly ash rich in KCl aerosols. By co-firing bituminous coal and straw it is possible to provide a fly ash where potassium mainly appears as potassium alumina silicates and minor amounts of sulfates.

A range of different studies with relevance for co-firing ash behavior has been conducted. This includes full scale-power plant co-firing experiments, some pilot-scale combustion studies, some studies on gaseous alkali reaction in fixed bed of minerals and theoretical equilibrium calculations on relevant ash systems.

Most experiments with co-combustion on power plants have focused on emissions, and operational problems. However, some fly ash related information can be extracted from

Danish full scale power plant experiments. Analyses of those data were done and can be seen in appendix B and in section 3.0 of this report.

Only a single pilot scale study with co-firing of straw and coal including detailed fly ash data was found. The results we obtained in our entrained flow reactor study were compared to this and similar trends was observed (appendix B).

To investigate the reaction between gaseous alkali and minerals several so called sorbent studies have been conducted. The results have mainly been relevant for cleaning of alkali from gasification gas, and in most cases the alkali containing gas is passed through a fixed bed of minerals. However most studies are done at 900° C or below and therefore do not cover the high temperatures relevant for co-firing.

Several studies have used equilibrium calculations to predict the speciation of potassium during co-firing. If sufficient sulfur is present it is predicted that at low temperatures (below 950° C) all potassium appears as sulfate, however this is not observed in real boilers, and it appears that a complex series of gas phase reactions do kinetically limit the formation of potassium sulfate. Equilibrium calculations on the mixed ashes indicate that a coal ash rich in Al and Si will provide the most efficient fixation of potassium in alumina silicates. Coal ashes with a high Ca content will not be efficient because the Ca is predicted to react with the alumina silicates and then prevent the alkali to react.

3.0 Entrained flow reactor co-firing tests and comparison with full-scale data

Co-firing combustion tests were conducted in the CHEC entrained flow reactor by firing different shares of straw with three different coals. Reference tests of unblended fuels were performed to establish a baseline for assessing the impact of co-firing on ash compositions. The collected ash samples included the deposit from a deposit probe, and fly and bottom ash samples. The compositions of the produced ashes were compared to the available literature data to find suitable scaling parameters that can be used to estimate the composition of ash from straw and coal co-firing.

In Figure 1 is shown the relative fraction of water soluble potassium in the fly ash as a function of the molar ratio of K/Si in the applied fuel mixture. Both measuring data obtained on power plant boilers (open symbols) and on the entrained flow reactor (closed symbols) are shown. The water soluble content of potassium is the potassium that appears as KCl and K₂SO₄, while the non water soluble potassium mainly are potassium silicate and potassium alumina silicates. It is seen that if a high surplus of silica is available only small amounts of salts will be present in the fly ash. Also, the curve in Figure 1 can be used to estimate the fly ash salt content if the inlet fuel composition is known. Reasonable agreement in fly ash compositions regarding total K and fraction of water soluble K was obtained comparing data from co-firing in the entrained flow reactor and on full-scale power plants. The total K content in fly ash is almost the same as that in fuel ash.

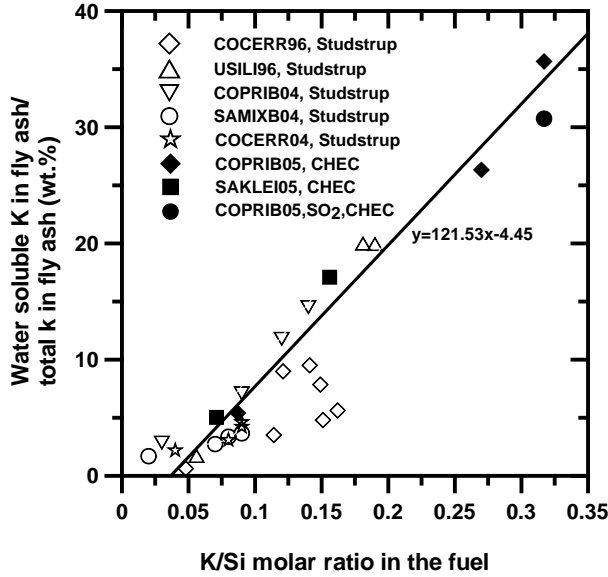


Figure 1. The ratio of water soluble K in the fly ash to total K in the fly ash for co-firing bituminous coal and straw as a function of the K/Si molar ratio of the applied fuel.

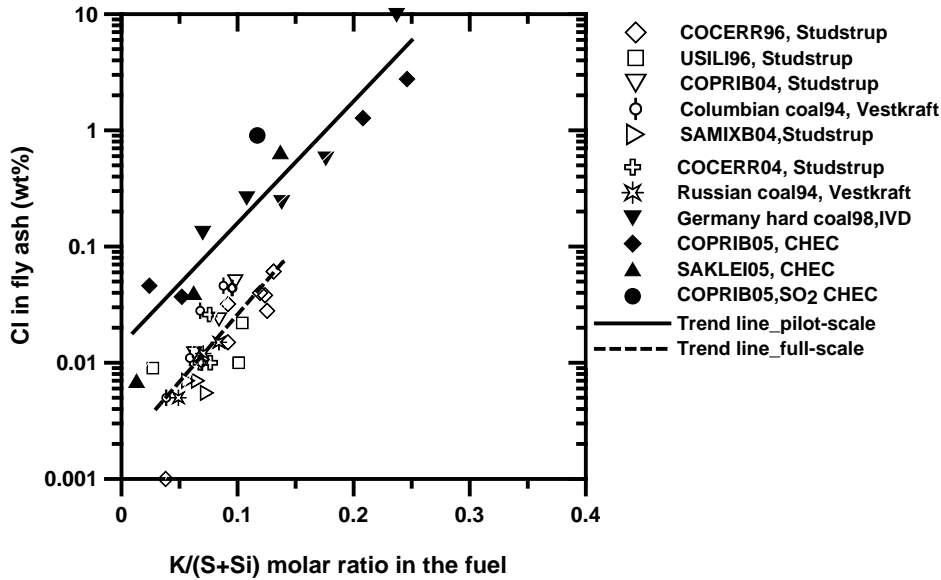


Figure 2. The content of Cl in the fly ash from co-firing bituminous coal with straw as function of the K/(S+Si) molar ratio of the applied fuel mix.

In the fly ash from the power plant tests co-firing straw and bituminous coal approximately 90% of the water soluble K appears as K_2SO_4 . While the fraction of water soluble K in form of K_2SO_4 in the fly ash increases almost linearly with the S/Cl molar ratio in the fuel mixture for the entrained flow reactor tests. The lower degree of sulfation

in the entrained flow reactor tests is probably caused by a short residence time in the temperature window 650 - 1000 ° C where the sulfation takes place.

The Cl content in the fly ash increases with the K/(S+Si) molar ratio of the fuel, as can be seen in Figure 2. The Cl content in the fly ash from full-scale tests is smaller than that from the entrained flow reactor tests.

The fraction of water soluble K in the fly ash from lignite/straw co-firing seems to be independent of the fuel K/Si molar ratio and is much larger than that in the fly ash from bituminous coal and straw co-firing. Lignite/straw co-firing also produces fly ash with relatively large Cl content. This is probably caused by the large content of calcium and magnesium in the lignite that reacts with silica so it is not available for reaction with potassium chloride.

The compositions of the collected fly ashes and deposit samples could be compared. Reduction of Cl and increase of S in the deposits compared to the fly ashes are observed and this could be attributed to sulfation of the deposits.

The findings in this work provide some implications for co-firing of straw with coal in pulverized fuel systems. To produce saleable fly ash and meet the requirement for fly ash used in concrete and cement production, and reduce the chlorine content in the deposit, coal with high Al and Si content should be used. On the other hand, co-firing may also be an attractive solution for lignite fired boilers that are designed for bad fuels and often the ash is not utilized. The fly ash properties can to some degree be estimated by the fuel composition and the scaling parameters developed in this investigation.

4.0 Kinetic study of potassium capture by coal minerals in a high temperature fixed bed reactor

The reactions between potassium chloride vapor and coal minerals were investigated in a lab-scale high temperature fixed bed reactor under well-defined conditions. The applied coal minerals included kaolin, mullite, silica, alumina, bituminous coal ash and lignite coal ash that were formed into long cylindrical pellets. Alumina pellets saturated with KCl were used as an alkali source and the applied pellet reaction temperatures were 900-1500°C. Weight loss of coal mineral pellets during heating without potassium in the gas were conducted as baseline tests and used to calculate the pellet weight gain after exposing it to the potassium vapor. An example of measuring results can be seen in Figure 3. There is shown the kaolin pellet weight as a function of residence time.

In Figure 4 the weight gain of different tested minerals are shown. A high weight gain means a large amount of potassium is bound. Metakaolin, formed by calcination of kaolin, conversion decreases with increasing temperature in the range of 900-1300°C and increases again with further increasing temperature up to 1500°C. The effect of reaction temperature on pellet weight gain could be attributed to melting and deactivation of the pellet, transformation of diffusion mechanism from gas diffusion to solid state diffusion

when the reaction temperature is increased from 900 to 1300°C and liquid diffusion when the temperature is further increased.

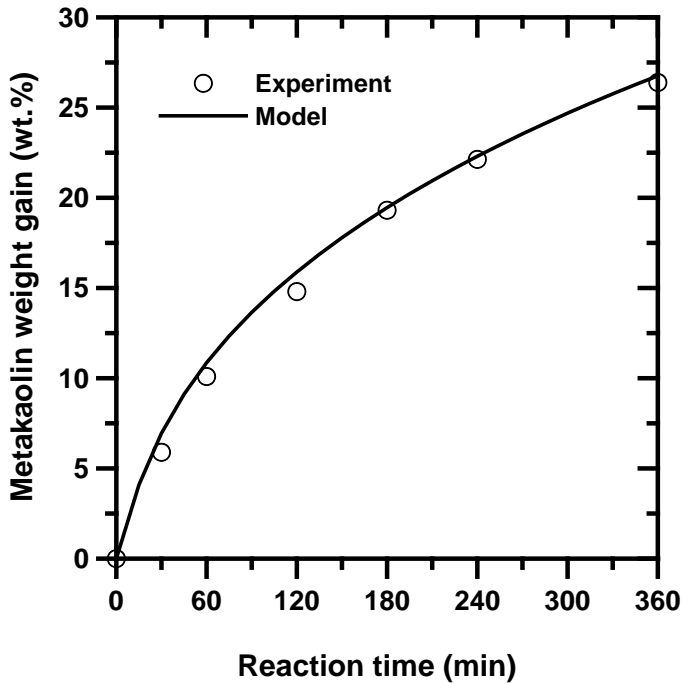


Figure 3. Metakaolin weight gain as function of reaction time. Kaolin pellets with a diameter of 1.56 mm were exposed to 1000 ppmv KCl at 900°C (a full conversion of the metakaolin corresponds to a weight gain of 41-42 wt%).

Metakaolin can be converted to mullite by high temperature treatment, and the formation of mullite has been proposed to decrease the capacity of kaolin to react with KCl. The fact that no reaction of mullite with KCl was observed at temperatures below 1300°C indicates that formation of mullite could be a deactivation mechanism of the kaolin pellet. However, the weight gain by mullite is only slightly smaller than that by kaolin in the temperature range of 1300-1500°C. Formation of mullite depends on many parameters such as heating temperature, rate and time. Only after a heating time of hours significant mullite formation can be observed. So it is expected that very limited amount of mullite is formed when kaolin powders are injected into a pulverized coal boiler, where a typical particle residence time is only a few seconds. Thus KCl mainly reacts with metakaolin in a straw/coal co-fired pulverized fuel boiler using kaolin as additive to capture potassium.

As seen on Figure 4 sand and alumina were not efficient to bind the potassium. The weight gain by alumina at 900 and 1000° C were caused by adsorption of KCl and not a reaction where HCl was released. Kaolin and bituminous coal ash that have both significant amount of Si and Al and show superior potassium capture capacity

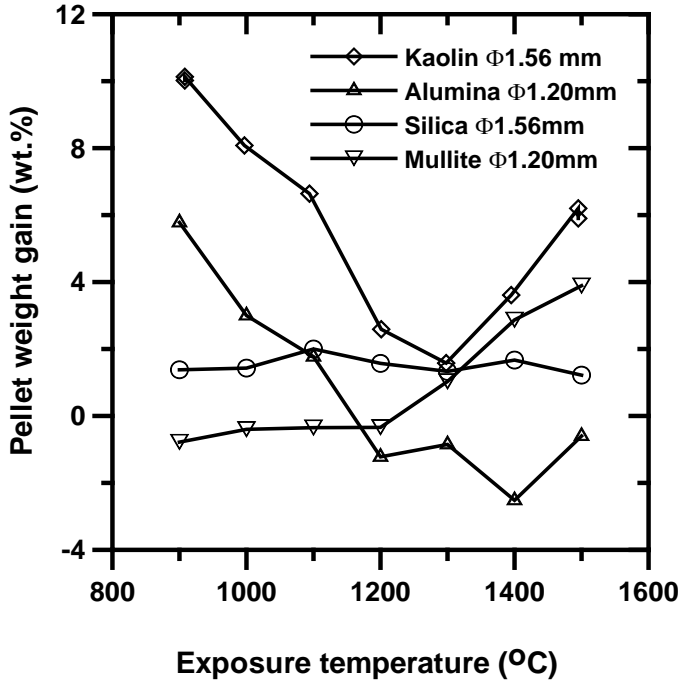


Figure 4. Weight gains of different sorbent pellets as a function of reaction temperature. Pellets were exposed to 1000 ppmv KCl for 1 h.

SEM-EDX analyses were conducted to study the element distribution inside the reacted pellets and the pore structure evolution during heating and reaction. Significant amount of Cl was detected in alumina pellet exposed to KCl. Almost no Cl was detected in all the others samples. This implies that capture of potassium by coal minerals applied in this work except alumina is obtained mainly by chemical reaction. An observed steep potassium profiles inside the reacted pellets indicate that there is significant transport resistance inside the pellet. Mullite formation was observed by SEM image of kaolin exposed to 1500°C.

A simple model was developed for the gas-solid reaction between the KCl vapor and metakaolin pellet at 900°C assuming no deactivation of the pellet and that external mass transfer can be neglected. The gaseous reactant is modeled by considering diffusion and reaction in the porous pellet, while the solid product is accumulated over time. The model can reasonably predict the pellet conversion as a function of KCl vapor pressure and reaction time (see Figure 3), and the radial concentration profile of captured potassium inside the pellet is well described.

5.0 Potassium capture by kaolin and fly ash powder in entrained flow reactor

To study the influence of local conditions on the reaction between gaseous KCl and coal minerals experiments were done on CHECs electrically heated entrained flow reactor, which can simulate the local conditions in suspension fired boilers. The experimental results were compared with model calculations to support the interpretation. This part of

the project work is preliminary in the sense that the model do not covers all the relevant temperatures and the experimental results do have some serious uncertainties. The experiments were planned to test the influence of changed temperature, residence time and KCl vapor concentration.

The degree of KCl reaction with kaolin in the entrained flow reactor experiments is determined by the fraction of water soluble K in the resulting particle product. Potassium that reacts with kaolin forms potassium alumina silicates that are not water soluble. However, the concentration of gaseous KCl available for the reaction with kaolin can only be determined if all injected KCl is evaporated. Experimental tests indicated that nearly complete evaporation was obtained if the temperature was 1100° C or above. However, analysis of SEM images of the product from 1100° C experiments indicates that even here some KCl has not been completely evaporated. The reason is presently not clear but it may be caused by some larger KCl particles or by a bad mixing between the hot gas and the injected KCl/kaolin mixture. However, with some precaution the following conclusions can be provided based on the experimental and modeling work:

- For particles bellow 20 μm at 900° C the kinetics determine the conversion rate and both external and internal transport limitations are not important.
- For experiments done at 1100° C with a molar ratio of K/Si=0.3 and a residence time of 1.07s approximately 80% of potassium from KCl reacted with kaolin.
- A changed temperature (1100-1300° C) or a changed amount of KCl (K/Si = 0.1 – 0.34) did only change the KCl conversion slightly.
- Si and Al rich coal ash seems to be less efficient to react with KCl compared to kaolin. However the applied coal ash had a larger particle size ($d_{50} = 22\mu\text{m}$) compared to the kaolin ($d_{50} = 10\mu\text{m}$).
- The kinetic rate constant of the reaction of KCl with kaolin has been determined to be larger for the entrained flow reactor experiments than the rate constant determined from fixed bed experiments on larger particles. Presently the reason for the observed deviation is not clear.

6.0 Application of the results for CFD calculations

It is wanted to account for the ash behavior during co-firing of biomass and coal by CFD models. A full mechanistic model that includes all interactions is not available today. Shortly stated the speciation of potassium to a high degree determines the fly ash properties and thereby also influence the deposit formation process. To model just the main reaction there needs to be accounted for the reaction between gas phase KCl and silica and alumina rich ash particles as well as the sulfation of KCl. In this project it has been possible to provide some guidelines (See section 3 and appendix B) regarding the speciation of potassium when co-firing straw and coal in full size boilers. However, it is important to realize, that the ash composition estimation is determined after the completed boiler processes, and also there are some significant uncertainties of the estimations. A possible way to deal with the CFD modeling of ash in a co-fired boiler is to assume that the potassium speciation is similar locally in the boiler as to the observed

exit fly ash potassium speciation. However, this ignores the time dependence of the reaction of KCl with coal ash particles and sulfur. Near the burners before the reactions have taken place, higher local concentrations of KCl could therefore be expected.

7.0 Conclusion

The properties of the ash from co-firing of coal and straw have a large influence on boiler operation, flue gas cleaning equipment and appropriate utilization of the fly ash. The straw ash contains high contents of potassium and chlorine that forms KCl during the combustion process. A high fly ash KCl content can cause increased ash deposit formation and boiler corrosion, deactivate SCR catalysts and prevent the fly ash from being used for cement or concrete production. By co-firing straw and coal potassium will to some degree form potassium alumina silicates and potassium sulfates that are less troublesome. Coal ash rich in Al and Si will provide the most efficient containment of potassium in alumina silicates

A study on the fuel composition influence on fly ash properties has been done by making entrained flow reactor experiments. By using the composition of the inlet coal and straw mixture it is possible to estimate the distribution of potassium alumina silicates, potassium sulfate and potassium chloride in the generated fly ash.

Fixed bed studies at temperatures from 900 to 1500° C on the reaction of vapor KCl with different minerals were performed. Kaolin and bituminous coal ash are efficient alkali getters, while lignite, sand and alumina do not efficiently react with KCl. For both kaolin and coal ash a minimum conversion was observed at temperatures of 1200 to 1300° C. The reason for this minimum is the transport properties of alkali in the particles. At low temperatures (<1200° C) the alkali mainly diffuse in the particle pores, at intermediate temperatures the pores close and condensed phase diffusion controls, and at high temperatures (>1300° C) the KCl diffuse in a melted phase.

Experiments with injection of small kaolin (approximately 20µm) and KCl particles in an electrically heated entrained flow reactor were performed to get a better understanding of the influence of the local conditions on the ash product from co-fired suspension boilers. The results had some uncertainties due to problems to accurately control KCl evaporation. The experiments indicate that for small particles (equal or below 20µm) at 900° C it is solely the kinetics that control the conversion rate.

8.0 Danish summery

Ved samfyring af kul og halm dannes en aske hvis kvalitet har stor betydning for drift af kedel og røggasrensningsanlæg og for genanvendelses mulighederne for flyveasken. Halm indeholder en høj mængde kalium og klor som danner KCl ved forbrændingen. En aske med et højt indhold af KCl kan give anledning til fyrrums aske belægninger, kedel korrosion, forgiftning af SCR katalysatorer samt umuliggør genanvendelsen af flyveakse til cement og beton produktion. Ved samfyring af halm og kul bindes kalium i nogen grad som kalium- aluminiumssilikater og kaliumsulfat som giver færre driftsproblemer.

En undersøgelse af indflydelsen af brændselssammensætning på aske egenskaberne er udført ved at lave samfyring af kul og halm på CHECs entrained flow reaktor. På basis af forsøgsresultaterne er det muligt ud fra elementarsammensætningen af den anvendte brændsels mix af kul og halm at estimere fordelingen af kalium mellem kalium- aluminiumssilikater, kaliumsulfat og kalium klorid i den dannede flyveaske.

Der er udført forsøg på fixed bed reaktor med at undersøge reaktionen mellem gasformig KCl og forskellige kul mineraler i temperatur området 900 til 1500 ° C. Kaolin og bituminøst kul aske var effektive til at reagere med KCl, mens brundkulsaske, sand og alumina ikke var effektive. For både kaolin og kulaske fandtes en minimum omsætning ved 1200 til 1300 ° C. Grunden til dette har baggrund i transportforholdene for KCl i partiklerne. Ved lave temperaturer (<1200 ° C) diffunderer KCl ind i partiklen via porerne, ved mellem temperaturer lukker porerne og fast fase diffusion begrænser reaktionen, og ved høje temperaturer (>1300 ° C) diffunderer KCl i en smelte.

En undersøgelse af kaolin partikler (middel størrelse på 20 µm) og KCl omsætning i den elektrisk opvarmede entrained flow reaktor er udført for at få en bedre forståelse af de lokale forholds indflydelse på askedannelsen i samfyrede suspensions kedler. Resultaterne fra denne delundersøgelse er behæftet med nogen usikkerhed da det ikke har været muligt helt at kontrollere fordamningen af KCl. Undersøgelsen indikerer at for små partikler (20 µm eller mindre) styre kinetik og omsætningsraten.

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